

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

10/018360

INTERNATIONAL APPLICATION NO.  
PCT/BR00/00065INTERNATIONAL FILING DATE  
June 23, 2000PRIORITY DATE CLAIMED  
June 23, 1999

## TITLE OF INVENTION

## AN APPARATUS AND PROCESS FOR PRE-HYDROLYSIS OF BIOMASS

APPLICANT(S) FOR DO/EO/US ---Daltro Garcia Pinatti, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau) b ☐ has been transmitted by the International Bureau (see Form 308) c ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2))
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau)
  - b. ☐ have been transmitted by the International Bureau
  - c. ☐ have not been made, however, the time limit for making such amendments has NOT expired
  - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4))
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98. (w/ copy of PTO-1449 and each reference cited therein and Int'l Search Rept)
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment  
☐ A SECOND or SUBSEQUENT preliminary amendment
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information.
  - a) Copy of PCT Publication WO 00/78446 with International Search Report (PCT/ISA/210)
  - b) Formal Drawing Set (included with international application)
  - c) PCT Request (Form PCT/RO/101)
  - d) Notification of Transmittal of The International Search Report or the Declaration (Form PCT/ISA/220)
  - e) PCT Demand (Form PCT/IPEA/401)
  - f) Invitation to Pay Additional Fees (PCT/ISA/206)
  - g) Invitation to Restrict or to Pay Additional Fees (PCT/IPEA/405)
  - h) Answer to Invitation to Restrict or to Pay Additional Fees (dated August 30, 2001)
  - i) Notification of Transmittal of the International Preliminary Examination Report (Form PCT/IPEA/416)
  - j) International Preliminary Examination Report (Form PCT/IPEA/409)

(Page 2)

U.S. DEPARTMENT OF COMMERCE, PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER  
33970R002TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371U.S. APPLICATION NO. (if known, see  
37 CFR 1.1) 10/01836017. ☒ The following fees are submitted:

CALCULATION

PTO USE ONLY

**Basic National Fee (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO ..... \$890.00  
 International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... \$670.00  
 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee  
 paid to USPTO (37 CFR 1.445(a)(2)) ..... \$760.00  
 Neither international preliminary examination fee (37 CFR 1.482) nor  
 international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$970.00  
 International preliminary examination fee paid to USPTO (37 CFR 1.482)  
 and all claims satisfied provisions of PCT Article 33(2)-(4) ..... \$96.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest  
claimed priority date (37 CFR 1.495(e)).

\$ -

Claims	Number Filed	Number Extra	Rate		
Total Claims	25 - 20 =	5	x \$18.00	\$ 90.00	
Independent Claims	2 - 3 =	0	x \$8400	\$ .00	
Multiple dependent claim(s) (if applicable)			+ \$280.00	00	
TOTAL OF ABOVE CALCULATIONS =				\$980.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$ 00	
SUBTOTAL =				\$ 980.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ -	
TOTAL NATIONAL FEE =				\$ 980.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)) The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property.				\$ .00	
TOTAL FEES ENCLOSED =				\$980.00	
				Amount to be refunded	\$
				charged	\$

- a. ☒ A check in the amount of \$980.00 to cover the above fees is enclosed  
 b. ☐ Please charge my Deposit Account No. 02-4300 in the amount of \$\_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.  
 c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required with respect to any deficiency in the above noted "Basic  
 National Fee", or credit any overpayment to Deposit Account No. 02-4300.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed  
 and granted to restore the application to pending status.

## SEND ALL CORRESPONDENCE TO:

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SIGNATURE

Dennis C. Rodgers - 32,936

NAME REGISTRATION NO.

Date: December 19, 2001

Atty. Dkt. No.  
33970R002

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Daltro Garcia Pinatti, et al.

International Application No.: PCT/BR00/00065

International Filing Date: June 23, 2000

U.S. Serial No.: To Be Assigned

Group Art Unit: To Be Assigned

Filed: : December 19, 2001 (Herewith)

Examiner: To Be Assigned

For: AN APPARATUS AND PROCESS FOR PRE-HYDROLYSIS OF BIOMASS

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to or concurrent with calculation of the filing fees, please amend this application as follows.

**IN THE CLAIMS**

Applicants have attached to this Amendment documents entitled "Amended Claims" and "Marked-Up Copy of Previous Claims". Please replace claims 7, 8, 9, 10, 12, 13, 14, 17, 18 and 19 with amended claims 7, 8, 9, 10, 12, 13, 14, 17, 18 and 19 as shown in the document entitled "Amended Claims".


REMARKS

Entry and consideration of this Preliminary Amendment is respectfully requested prior to or concurrent with calculation of the filing fees. This Preliminary Amendment is being filed to remove the multiple dependent claim to avoid the surcharge.

Examination on the merits is awaited.

Respectfully submitted,

SMITH, GAMBRELL & RUSSELL, LLP

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December 19, 2001

10/018360  
JC13 Rec'd PCT/P10 19 DEC 2001

MARKED UP COPY OF CLAIMS

7. An apparatus according to [any one of claims 1 – 6] claim 1, characterized in that the external coating (1) and the internal coating (2) are made of corrosion resistant material.
8. An apparatus according to [any one of claims 1, 6 or 7] claim 1, characterized in that its external coating (1) and internal coating (2) are made of microbonded carbon steel and refractory material, respectively.
9. An apparatus according to [any one of claims 1, 6, 7 or 8] claim 1, characterized in that the external coating (1) and the internal coating (2) are mounted by simple juxtaposition, free from welding.
10. An apparatus according to [any one of claims 1 – 9] claim 1, characterized by comprising devices for detecting and monitoring the vacuum between the external coating (1) and the internal coating (2).
12. An apparatus according to [any one of claims 10 or 11] claim 10, characterized in that the detection of microcracks is made in a continuous way.
13. An apparatus according to [any one of claims 10 – 12] claim 10, characterized in that helium gas is introduced into the reactor for detection of microcracks in the internal coating.
14. An apparatus according to [any one of claims 7 – 10] claim 7, characterized in that the microleakage detectors are coupled to the vacuum pump (15).
17. A process according to [claims 15 or 16] claim 15, characterized in that the purging of steam from the pre-hydrolysis device maintains the temperature around 150° C - 170° C.
18. A process according to [any one of claims 15, 16, or 17] claim 15, characterized in that the purging of steam from the pre-hydrolysis device maintains the temperature preferably around 106° C.



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JC13 Rec'd PCT/PTO 19 DEC 2001

AMENDED CLAIMS



7. An apparatus according to claim 1, characterized in that the external coating (1) and the internal coating (2) are made of corrosion resistant material.
8. An apparatus according to claim 1, characterized in that its external coating (1) and internal coating (2) are made of microbonded carbon steel and refractory material, respectively.
9. An apparatus according to claim 1, characterized in that the external coating (1) and the internal coating (2) are mounted by simple juxtaposition, free from welding.
10. An apparatus according to claim 1, characterized by comprising devices for detecting and monitoring the vacuum between the external coating (1) and the internal coating (2).
12. An apparatus according to claim 10, characterized in that the detection of microcracks is made in a continuous way.
13. An apparatus according to claim 10, characterized in that helium gas is introduced into the reactor for detection of microcracks in the internal coating.
14. An apparatus according to claim 7, characterized in that the microleakage detectors are coupled to the vacuum pump (15).
17. A process according to claim 15, characterized in that the purging of steam from the pre-hydrolysis device maintains the temperature around 150° C - 170° C.
18. A process according to claim 15, characterized in that the purging of steam from the pre-hydrolysis device maintains the temperature preferably around 106° C.
19. A process according to claim 15, characterized in that the pre-hydrolysis is effected during about 30 minutes simultaneously with oscillation and purging of steam.

**Title: "AN APPARATUS AND PROCESS FOR PRE-HYDROLYSIS OF BIOMASS"****Field of the invention**

This invention relates to an apparatus, specifically a reactor, and to a process for pre-hydrolysis of any kind of biomass (wood, bagasse, straw, grass, vegetable residues, organic garbage, etc.) to obtain commercial products, such as cellulignin and sugar solutions, pre-hydrolysate layers, containing xylose, glucose, mamose, galactose, arabinose, acethyl-ics, uranic acids, etc. This invention further enables one to manufacture reactors for the digestion of minerals, such as ilmenite, anatasie, columbite, pyrochlore, zirkonite, etc.

**Description of the prior art**

Chemical reactors are devices that are defined by a variety of processes for transforming materials, such as chemical, metallurgical, thermal, biotechnological, pharmaceutical materials, etc. Reactors are classified by three criteria:

a) classification according to vessels and flows: 1st) batch reactor; 2nd) semi-continuous reactor; 3rd) tank reactor with continuous mixer – RTMC; 4th) RTMC in series; 5th) tubular reactor; and 6th) recycling reactor.

b) classification according to the existing phases: 1st) reactors for gaseous phases; 2nd) reactors for liquid phases; 3rd) reactors for liquid and gaseous phases; 4th) reactors with solid catalysts; 5th) non-catalytic reactors involving solids (gas-solid, liquid-solid, and reactions of gaseous phases; 6th) reactors for electrochemical processes; 7th) reactors for biological processes; 8th) reactors for photochemical and radiochemical processes. The non-catalytic gas-solid and liquid-solid reactors with which, by way of example, the reactor of this invention should be compared, are listed below.

b.1) non-catalytic gas-solid reactor: retort (tower-type reactor), movable bed reactor, multiple bed reactor, rotary oven reactor, fluid bed reactor, recirculating flow reactor, dust calciner (dust spray).

5 b.2) non-catalytic liquid-solid reactors: tank with a mixer (batch, semi-continuous, cascade - percentage of solids limited by the power of the mixer), tank with recirculation of liquids, rotary drum, fluid bed, kneading machine, immersion-press type reactor, helical conveyor, cradle-type reactor, rotary oven reactor.

10 c) Classification according to the movement condition of the solids presented in Table 1. The reactor of this invention tends towards the characteristics of a fluid bed, albeit movable, with the following values: reaction device (tank), movement of the solids (gravitational), gas/liquid-solid flow (counter current), particle diameter (mm to cm), time of retention of the solids (minutes), time of retention of the gas (seconds), rate of heat and mass transfer (high), temperature control (good), yield in terms of volume and time (high).

15 Other important characteristics of reactors are the materials used to manufacture them. Table 2 gives the basic materials with their respective advantages and disadvantages for high corrosion conditions. The structural materials and those resistant to corrosion, even when used in making reactors, each presents a single disadvantage, which this invention eliminates by making the reactor with a shell and structure made of carbon steel and a coating of special materials (refractory, superalloys, stainless steel and plastics, etc.).

20 Specifically, the main biomass reactors are of the following types: screw (low volume occupation percentage), tower (high L/S - liquid-solid ratio, tank/percolation (high L/S ratio and plug flow (high L/S ratio). All the types of reactor have complex biomass feed and discharge systems. This invention compacts biomass in the reactor (high rate of volume occupation of the reactor), processes the biomass with low L/S ratio = 2, provides feed with a  
25 simple helical feeder and immediate discharge due to the fact that the reactor has a large cover and can be divided into small-size and medium-size reactors.

30 One disadvantage of the reactors of the prior art is that they are subject to implosion due to the fact that their construction does not permit a perfect juxtaposition between the shell and the coating, and there is a vacuum inside the reactor, caused, in most cases, by steam condensation. This invention prevents implosion through the vacuum maintained between the coating and the shell, so as to allow them to be properly juxtaposed.

Another disadvantage of the conventional reactors is the impossibility of continuously and precisely detecting microleakage in the coating. This invention permits the precise detection of microleakage before the occurrence of leakage of corrosive liquids into the steel shell of the reactor. This allows the reactor to be further used, even with microfailures, by adequately programming it for use.

The reactors used in high-corrosion applications do not utilize carbon steel in the shell and tend to be made of expensive monolithic materials. By enabling the identification of microleakages, this invention detects the conditions for accelerated corrosion of the microbonded carbon steel, and this detection facilitates the use thereof, which brings about a significant reduction in the costs of manufacturing the reactor.

The reactors of the prior art are built from thick materials, in order to achieve greater resistance to corrosion. Therefore, sometimes the thickness of the metal in the construction of the reactors has a direct relationship with the safety, and the utilization of very thick plates makes their transportation to areas where there is raw material for their use impossible. The reactor of this invention provides perfect control for detection of failures and allows lighter materials to be used, which reduces the total weight of the reactor and consequently facilitates its transportation.

US Pat. 5,338,366 refers to a method and apparatus for pre-hydrolysis of biomass that, among other features that are different from this invention, is very heavy and so remains in a stationary position, which requires raw biomass to be transported to it. In addition, the pre-hydrolysis of biomass is made in various pieces of equipment, which increases the consumption of energy for carrying it out and renders the production process expensive. This invention, in addition to eliminating these drawbacks, facilitates a high concentration of sugar in the pre-hydrolysate, thus reducing the costs of the following processes, and enables one to use deionized water due to the low liquid/solid ratio for the production of clean catalytic cellulignin fuel for use in gas turbines.

US Pat. 5,411,594 deals with the hydrolysis of lignocellulose biomass for the production of a single sugar solution and lignin residues. The whole hydrolysis is carried out in two stages (hemicellulose and cellulose) in a continuous reactor and has an L/S ratio of 5:10 with a maximum output of 65%, and, due to the high L/S ratio, there is a complex heat-recovery system. This invention implements the whole process, since it carries out the pre-hydrolysis of hemicellulose in a batch-type reactor with an L/S ratio = 2 and has an output of 100% (maximum utilization of raw material): recovery of cellulignin 80% and pre-hydrolysate

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20%. The recovery of heat takes place only when discharging the pre-hydrolysate, pre-heating the acidic solution and water in the boiler.

Table 1 – Classification according to the state of movement of the solids


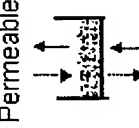
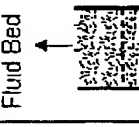
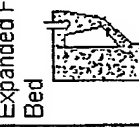
Reactor type	Fixed bed		Fluid bed		Transport
	Upper flow 	Permeable 	Fluid Bed 	Expanded Fluid Bed 	
Typical reaction devices	Multiple cradle Rotary furnace Drying belt	Vertical furnace Movable grid Burning on grid Furnaces	Fluid roaster Fluid bed roaster Multi-stage Fluid bed Furnace	Circulating fluid bed	Flash drying Pre-heater Fusion cyclone Burner
Movement of solids	Mechanical	Gravitational	Gravitational	Gravitational	Gravitational
Gas/solid flow	Parallel stream Counter-current Crossed current	Parallel flow Counter-current in stages Crossed current	Mixed flow Counter-current in stages Crossed current	Parallel currents Mixed flow: recycling Stages in counter-current	Parallel currents Mixed flow: recycling Stages in counter-current
Particle diameter	Small to very large (mm/m)	Medium to very large (cm/m)	Small and medium (mm/cm)	Very small to small (mm/mm)	Very small (mm)
Retention time of the solids	Hours - days		Hours	Minutes	Seconds and fractions
Retention time of the gas	Seconds		Seconds		Fractions of seconds

Table 1 - cont.

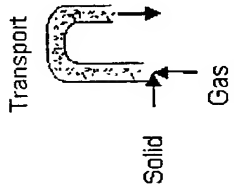
Reactor type	Fixed bed			Fluid bed			
	Transfer rate of heat and mass	Very low	Low – medium	High	Very high	Very high	
	Temperature control	Very good	Poor – medium	Good	Very good	Medium - good	
	Output in volume and time	Very low	Medium	Medium High	High	Very high	

Table 2 – Basic Materials Used in the Manufacture of the Reactors

MATERIALS		ADVANTAGES	DISADVANTAGES
<b>Structural materials</b>	Mo (C-1/2Mo) carbon steel, Cr-(1 ¼ Cr- ½ Mo, 2 ¼ Cr – 1Mo, 5 Cr-1Mo) steel, stainless (405, 410, 304, 316, 321, 347, 309, 310, steel resistant to heat (HH, HK, HP), monel, brass, bronze, aluminum, etc.	<ul style="list-style-type: none"> <li>·Low cost</li> <li>·Availability</li> <li>·Resistance to abrasion</li> <li>·Ease of manufacture</li> <li>·Mechanical resistance (strength) to medium temperature</li> <li>·Recyclable</li> <li>·Ductility</li> </ul>	<ul style="list-style-type: none"> <li>·Low resistance to corrosion</li> </ul>
<b>Metals resistant to corrosion</b>	Cr-Mo (9Cr-½ Mo), steel, inconel, incoloy, hastelloy, duplex allows, Fe-Si, stainless, ferritic, Ni (3½ Ni, etc.) steels, lead, Cu-Ni (70/30, 90/10, etc.), refractory metals (Ti, Zr, Nb, Ta, W, Mo and their alloys) and proprietary alloys	<ul style="list-style-type: none"> <li>·Medium and high resistance to corrosion</li> <li>·Availability</li> <li>·Resistance to abrasion</li> <li>·Ease of manufacture</li> <li>·Mechanical resistance to high temperature</li> <li>·Recyclable</li> <li>·Ductility (except for Fe-Si).</li> </ul>	<ul style="list-style-type: none"> <li>·High cost</li> </ul>
<b>Thermoplastic materials</b>	Teflon (260°C), chlorinated polyester (121°C), polyvinylidene fluoride (121°C), polyvinylidene chloride (93°C), polypropylene PP (90°C), polyethylene PE (93°C), polyvinyl chloride – PVC (71°C), chlorinated polyvinyl chloride and reinforced PVC (99°C)	<ul style="list-style-type: none"> <li>·Low cost</li> <li>·Availability</li> <li>·Ease of manufacture</li> <li>·High resistance to corrosion</li> <li>·Recyclable</li> <li>·Ductility</li> </ul>	<ul style="list-style-type: none"> <li>·Low resistance to abrasion</li> <li>·Low mechanical resistance (strength)</li> </ul>
<b>Elastomers</b>	Natural rubber (66°C), ebonite (82°C), hypalon (93°C), neoprene (93°C), buthylic rubber (93°C), hycar (121°C), viton (204°C).	<ul style="list-style-type: none"> <li>·Low cost</li> <li>·Availability</li> <li>·Ease of manufacture</li> <li>·High resistance to corrosion</li> <li>·Ductility</li> </ul>	<ul style="list-style-type: none"> <li>·Low resistance to abrasion at medium temperature</li> <li>·Low mechanical resistance (strength)</li> <li>·Non-recyclable</li> </ul>
<b>Reinforced heat cured plastics</b>	Glass fiber/polyester (93°C), asbestos/epoxy (149°C), glass fiber glass/epoxy (149°C), asbestos/fenolic (149°C), asbestos/furanic (149°C), glass fiber/furanic (93°C), carbon fiber/furanic (93°C).	<ul style="list-style-type: none"> <li>·Availability</li> <li>·High resistance to corrosion</li> <li>·Ease of manufacture</li> <li>·High mechanical resistance (strength)</li> <li>·Ductility</li> </ul>	<ul style="list-style-type: none"> <li>·High cost</li> <li>·Low resistance to abrasion</li> <li>·Non-recyclable</li> </ul>
<b>Special non-metallic materials</b>	Cement or concrete, reinforced cement, antiacid refractories, graphite bricks, impermeable graphite, glasses and vitrification, wood and refractories	<ul style="list-style-type: none"> <li>·Low cost</li> <li>·Availability</li> <li>·High resistance to abrasion</li> <li>·Ease of manufacture</li> <li>·High resistance to corrosion</li> <li>·Mechanical resistance to high temperature</li> </ul>	<ul style="list-style-type: none"> <li>·Low mechanical resistance (strength)</li> <li>·Fragility</li> <li>·Non-recyclable</li> </ul>



## Summary of the invention

This invention refers to an apparatus, more specifically a reactor or boiler, built with technology that enables use in highly corrosive environments. The new technology consists of inserting a vacuum between its outer coating, the "shell", and the inner coating, so as to utilize microbonded carbon steel in the shell and structure of the reactor, and special materials, especially refractory metals (Ti, Zr, Nb, Ta, and their alloys) for the inner coating. The vacuum with the coating of refractory material further permits the use of high-resistance (750 MPa) microbonded steel in the manufacture of the ultralight shell of the "egg-shell"-type reactor, enabling oscillation at higher frequencies with higher homogenization of the product and shorter reaction time thereof.

The satisfactory vacuum level is below 1mm of Hg (1,000  $\mu$ m), so that the refractory metal coating will not suffer implosion, and so that it is possible to use a helium leakage detector coupled between the reactor and the vacuum pump for detecting and measuring leakage through the microcracks of the welds. Leakage rates of  $10^{-4}$  Ncm<sup>3</sup>/min indicate a satisfactory level and leakage rates 100 times higher ( $10^{-2}$  Ncm<sup>3</sup>/min) indicate the need for repair of the welding cracks or those developed during operation of the reactor. Another characteristic of the invention is the possibility of maintaining and maybe replacing the coating of refractory metal altogether, with high aggregated value for recovery of these scrapped metals due to the carbon steel reactor's juxtaposed manufacture, maintained by the vacuum and without welding to the shell.

The vacuum between the shell of the reactor and the coating maintains the thin coating of special metal juxtaposed to the steel shell, preventing the implosion of the reactor, even when there is vacuum inside it, due to the condensation of steam and other causes. The use of vacuum, among other advantages, also permits continuous or intermittent detection of microleakage in the coating of the reactor by injecting helium gas into the reactor and detecting with a leak detector) in the vacuum pump.

Due to this characteristic, this invention is called "failsafe-type reactor", by means of which one detects and measures microleakage in periods of days or months before the occurrence of leakage of corrosive liquids into the shell of the carbon steel. This characteristic enables one to use the reactor even with microfailures, and to program its repair or replacement after the industrial session or campaign has finished. One should note the significance of this characteristic of the invention for enabling one to use carbon steel in the re-





3) reactor - main object of the invention, where the processes of biomass hydrolysis, mineral digestion or any other chemical or thermochemical processes of any material are developed;

4) heat-exchanger - having three function, namely: a) recovery of the heat while discharging the pre-hydrolysate, b) pre-heating of the acidic solution, and c) pre-heating of the steam-generating water in the boiler;

5) tank or washing cart -where the cellulignin (or mineral) is washed to the desired extent, the pre-washing being recovered as pre-hydrolysate and the other washings being neutralized and treated in a stabilization pond prior to discharge into streams or for use in fertilization, etc.;

6) tank of pre-hydrolysate, either stationary or installed on carts - storing of the first product;

7) cellulignin or mineral dryer - drying of the second product;

8) cellulignin or mineral grinder - grinding of the second product;

9) silo, either stationary or installed on carts - storing of the second product.

The invention defines a new technology of manufacturing chemical reactors for processes in highly corrosive environments. Figure 2 illustrates in detail a reactor built with the technology of this invention and, in addition, shows all the components of an ordinary reactor for better understanding.

The conditions of internal corrosion of the reactor for different materials, temperature and acid content are given in Table 3, whence the following conclusions are drawn: 1) due to its high corrosion rate, stainless steel can only be used at high temperatures for a very short period of time; 2) it is possible to use commercial-grade Ti for the conditions of pre-hydrolysis of biomass ( $T = 15^{\circ} \text{C}$ , 1.5%  $\text{H}_2\text{SO}_4$ , 0.62 MPa), since this is a reactive material and passivates with sugar generated by the hydrolysis itself; 3) for the conditions of total hydrolysis of biomass ( $T = 190^{\circ} \text{C}$ , 1.5%  $\text{H}_2\text{SO}_4$ , 2.8 MPa) it is necessary to use NbTi alloys (example: Nb44%Ti) with a melting point  $T = 1,830^{\circ} \text{C}$  permitting easier welding than pure Nb, which has a melting point of  $T = 2,500^{\circ} \text{C}$ ; 4) for the conditions of mineral digestion ( $T = 150^{\circ} \text{C}$ , 60%  $\text{H}_2\text{SO}_4$ ,  $P = 0.6 \text{ MPa}$ ), it is necessary to use Nb40%Ta alloy, the corrosion rate

of which is in the order of 100 mm/year. Above 40% Ta, the alloys become expensive due to the need for using thantalite mineral instead of the columbite in the production of NbTa alloy.

**Table 3 - Corrosion Data for the Conditions of Pre-hydrolysis, Hydrolysis of Biomass and Mineral Digestion (mm/year)**

	Biomass			Mineral		
		Pre-hydrolysis	Hydrolysis	Mineral digestion		
T°C X% H <sub>2</sub> SO <sub>4</sub>	100°C 1%	150°C 1.5%	190°C 2%	143°C 60%	197°C 80%	Cost of material US\$/kg
SS 316	3,550	∞	∞	∞	∞	8
Ti	2,500	19,000	∞	∞	∞	50
Hastelloy	25	—	250	> 5,000	∞	40
Nb	0	4.5	< 25	574	31,761	50
Nb20%Ta	—	—	< 1	367	19,243	50
Nb40%Ta	—	—	—	67	4,093	50
Nb60%Ta	—	—	—	22	916	3,200
Nb80%Ta	—	—	—	3.4	275	410
Ta	0	< 1	< 1	0.1	111	500
Ti 1% H <sub>2</sub> SO <sub>4</sub> 7.2% Wood		100				

5

The details of figure 2 present the method of welding the refractory metal coating *in situ* and juxtaposed to the shell of the carbon steel reactor, without the former becoming molten or contaminating the refractory metal. Protections rings or plates of the same metal as the coating are placed on the welding of the parts and edges. The welding is carried out with plasma with inert-gas protection (helium or argon), guaranteeing interstice levels (C, O, N, H) within the norms of the initial material. As to the metallurgical characteristics, there is a growth of grains in the welded zones, decreasing the strength, mainly the fatigue strength. This decrease is acceptable, since the coating works in compression regime, and there is an increase in the coating in regions under traction regime. The construction of the reactor having a bipartite structure with a slight conicity at the cylindrical parts allows much of the welding to be carried out outside the carbon steel shell and only the junctions of large parts and edges to be welded *in situ*. It is also possible to recover significant portions of the coating, in case it is necessary to replace it, by virtue of the ease of disassembling it, thus recovering part of its cost as scrap of high value. The special metals enable the use of other acids, in addition to H<sub>2</sub>SO<sub>4</sub> (HCl, HNO<sub>3</sub>, etc.), provided that the effective pH is similar to the levels of the solutions of Table 3.

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Another feature of this invention is the use of elastomer rings (voton, silicone, teflon, and others) having a circular or trapezoidal cross-section on all the covers, connections and vacuum sealing in the coating. The sizing of the sealing rings follow standards of pressure and vacuum sealing. The type of ring is chosen in function of the temperature.

- 5 When processing minerals or biomass, the temperature usually is around 200° C, and the ring chosen is made of viton. On the other hand, for average temperatures, the ring should be of teflon/glass fiber/carbon fiber, the metallic one being most recommended for high temperatures.

- 10 In addition to biomass and minerals, it is possible to process any type of material in the "failsafe type reactor" (polymerization, foodstuffs, medicaments, synthesis of products, etc.), provided that the conditions of corrosion of the coating are respected. In highly aggressive conditions, one uses Ta, either pure or doped with platinum, which are insuperable materials compared with any other commercial material. For less aggressive conditions, the "failsafe" technique permits the use of lower quality noble coatings, mentioned in Table 2  
15 (stainless materials, nickel alloys, thermoplastics, elastomers, reinforced thermocured plastic, etc.), provided that the conditions of temperature, pressure, corrosion, abrasion, and strength of the material are respected.

- 20 The external conditions of corrosion of carbon steel are more aggressive at the moment of discharge of the products (cellulignin, minerals, etc.). Steams were condensed at the moment of discharge, their pH was measured, and various steels painted with bituminous epoxy paint were tested.

Table 4 gives the comparison of the costs/m<sup>2</sup> of the reactors coated with Ti, Nb and monolithic made of stainless steel and hastelloy. In addition to the technical superiority, they have lower costs than the monolithic reactors.

25 **Table 4 – cost of the materials used in the construction of the reactor/m<sup>2</sup>**

Coating Type	Material	Total Weight	Price/kg	Total Price	Final Price R\$/m <sup>2</sup>
Titanium	Steel plate 12 mm	91 kg	R\$ 1,00	R\$ 91,00	R\$ 379,00
	Ti plate 2 mm	9 kg	R\$ 32,00	R\$ 288,00	
Niobium	12 mm steel plate	91 kg	R\$ 1,00	R\$ 91,00	R\$ 1.211,00
	Nb plate 2 mm	16 kg	R\$ 70,00	R\$ 1.120,00	
Stainless steel	12 mm plate	91 kg	R\$ 16,00	R\$ 1.456,00	R\$ 1.456,00
Hastelloy	12 mm plate	91 kg	R\$ 32,00	R\$ 2.912,00	R\$ 2.912,00

The main characteristics of this invention are shown in figure 2, and Table 5 gives the caption of the parts and components of the reactor and of the feeder.

The reactor body is composed of the cylindrical portion 1.1, cap 1.2, inlet nozzle 1.3, inlet cover 1.4, conical sector 1.5, circular or radial sliding ring with wedges or pins 1.6, discharge cover with support of the wedge 1.7, valve connections, meters, accessories, etc. 1.8, hinge 1.9, articulation and hydraulic cylinder for closing the cover 1.10, hydraulic cylinder for closing and opening the wedges 1.11. The bipartition of the reactor is illustrated in detail A, which enables the assembly and disassembly of the special metal coating without welding or unwelding the steel shell of the reactor. For small reactors, the cover is displaced for bipartition, the conical sector being eliminated (for very small reactors, the shell and the coating may be juxtaposed only by fitting, without the need for welding). The cylindrical body is slightly conical to facilitate the assembly and disassembly of the coating. The latter is welded, in great part, prior to the assembly, the parts shown in details A - F remaining to be welded within the reactor shell. This technology is fundamental to make possible the welding close to the steel body of the reactor (melting point of 1760°) of the special metals having a high melting point (1800° C - 3100° C), preventing the contamination thereof with Fe. The opening and closing of the cover is done by means of two hydraulic systems, the first one commanding the internal-pressure support wedges of the reactor, maintaining the confinement pressure of the sealing ring (o-ring) of viton of the acidic solutions. This sealing ring supports for months or years the repetitive opening and closing during the operations.

The tilting system is composed of structure 1.12, pivot 1.13, and hydraulic cylinder 1.14. The latter is utilized to tip and shake the reactor during the operation of discharging the cellulignin, since it is a solid material. The horizontal motion system is composed of a cart 1.15 and a hydraulic cylinder 1.16. Alternately, the reactor may be fixed and the feeder may be horizontally moved. The fixed structure 1.17 supports the reactor and the feeder, and thereby the reactor can be detached from the cart to the support pillars (see figure 2.d). The turning oscillation system is composed of chain 1.18 and a hydraulic motor 1.19 commanded by micro-switches 1.20, which revert the rotation at pre-determined angles. The security of the turning oscillation system is given by the length of the chain, which escapes from gear of the hydraulic motor if the micro-switches fail.

The special metal coating 2.1 and 2.2 is made according to the details A - F. The main stresses on the coating occur on the inlet nozzle at the moment of loading of the reactor and on the cylindrical body, due to the movement of the turning oscillation system. The

stresses are low, and the life time of the coating longer than ten years is determined by the fatigue failure. The sealings are made with an elastomer ring on the discharge cover 2.3, in the bipartition 2.4, between the coating and the reactor shell 2.5. The protection against the melting of the steel and the contamination of the refractory metal weld with Fe is done with sacrifice rings of refractory metal 2.6.

The connections and valves of the reactor are intended for the entrance of water and acidic solution 3.1, entrance of steam 3.2, exit of steam 3.3, vacuum in the reactor body 3.4.1, in the conic sector 3.4.2, in the cover 3.4.3, discharge of the hydrolysate 3.5, valve for collecting pre-hydrolysate for analysis 3.6. The entrance of vapors is at the lower portion and they are distributed by a perforated tube. The entrance of liquid (water or acidic solution) is at the upper portion. Obviously, inlets for liquids and vapors do not present any problem of clogging. The steam outlet is at the upper portion through a perforated pipe, and the hydrolysate discharge is located at the lower portion at the conic sector, which is protected by perforated plate inside the reactor to avoid clogging. A sporadic steam return is foreseen on the plate and perforated tube for unclogging the steam outlet through a by-pass valve between the steam inlet and outlet, after the flexible tube for entrance of steam 3.7 and 3.8. Alternatively, one may use a rotary scraper for the perforated plates. The connections and valves are connected to the inlet supports of the flexible rotation tubes 4 by rigid pipes.

The flexible rotation tubes 5 are constituted by various units: water and acidic solution inlet 5.1, steam inlet 5.2, steam outlet 5.3, vacuum 5.4 and others. The maximum rotation permitted is  $\alpha = \pm 45^\circ$  C, so that no liquid will flow through the steam outlet. The level of the acidic solution is maintained below the water line (figure 2.d), so that no liquid will flow out. In case the steam outlet is below the liquid line, one resorts to electric commands of the steam outlet valve 3.3 for closing it, whenever the liquid limit line is exceeded. In general, these electric commands are unnecessary because the oscillating turn of  $45^\circ$  is sufficient to wet the whole biomass, homogenize the liquid and solid mass, and avoid preferred ways in the hydrolysis. The supports of the outlets of the flexible rotation tubes 6 are placed at the upper portion of the reactor.

The intermediate piping 7 are constituted by the same components of the flexible rotation tubes 7.1 - 7.4 and interconnect the outlets of the flexible rotation tubes to the inlets of the flexible tilting tubes.

The flexible tilting tubes 8 are constituted by the same components as the intermediate piping 8.1 - 8.4 and are designed for enabling one to tilt the reactor with its support



structure for discharging of the cellulignin. The outlet of the flexible tilting tubes are connected to the fixed piping 9.1 - 9.4. The latter connect the flexible tilting tubes to the set of valve pipes 9.5 installed on the control panel located beneath the feeder 16.

5 The vacuum sensors 10 are constituted by four units: reactor body 10.1, conic sector 10.2, reactor cover 10.3, and the piping of the vacuum pump 10.4. The closing of the pertinent valves and the viewing of the vacuum drop enable one to determine a possible leakage in the special metal coating.

10 The pressure gauge 11 is of the diaphragm type, in order to resist acidic mediums, and the temperature gauge 12 is protected by a protection shaft of the same material as the coating.

15 The hydraulic system 13 drives the following units in this order: hydraulic motor of the helical feeder 14.1, motion hydraulic cylinder 1.16, hydraulic cylinder of the closing cover 1.10, hydraulic motor of the oscillating rotary system 1.19, hydraulic tilting cylinder 1.14, hydraulic cylinders for opening the wedges 1.11. Please note that there is no simultaneity of any operation, the higher power prevailing, which is that of the hydraulic motor of the helical feeder 14.1.

20 The feeder is composed of a hydraulic motor 14.1, a semi-axle of the propeller 14.2, feeder propeller 14.3, feeder cradle 14.4, a conical feeder nozzle 14.5, and a coil 14.6. The feeder should fill the reactor in a period of 10 minutes. It is built of microbonded carbon steel, protected with bituminous epoxy paint. The space below the feeder is occupied by the control panel 16 (liquids, steams, meters, electric system, etc.), a hydraulic system 13, a vacuum pump 15, a leakage detector 17, work tools and working devices, etc.

25 The fixed structure of the reactor and the feeder accommodate in a standard cart with a platform located at 960 mm from the ground 18, maximum height of the lower equipment at 4.400 mm and within the road standards. The equipment is transported to biomass courts, where it is raised with hydraulic jacks and supported on beams and pillars at the desired processing height (figure 2.e). Alternatively, it can be operated on the transport cart itself.

30 The complementary pieces of equipment of the reactor are: heat exchanger 19, water pressure pump 20.1 and acidic solution discharge 20.2, water deionizer 21, boiler 22, and support structure 23. The latter is transported on standard carts 18, elevated and supported in the same way as the explained before.

**Table 5 – Key of the Reactor and Feeder Parts**

**A – 1st Structure (1st cart)**

	1	– reactor shell and structure
	1.1	– cylindrical body
5	1.2	– cap
	1.3	– inlet nozzle
	1.4	- inlet cover
	1.4.1	– cover
	1.4.2	– hydraulic cylinders
10	1.5	– conical sector
	1.6	– sliding ring with wedges
	1.7	– discharge cover with support for the wedges
	1.8	– connections
	1.9	– hinge
15	1.10	– articulation and hydraulic cylinder cover opener
	1.11	– hydraulic cylinder for closing/opening of wedges
	1.12	– tilting structure
	1.13	– tilting pivot
	1.14	– tilting hydraulic cylinder
20	1.15	– movement cart
	1.16	– horizontal movement hydraulic cylinder
	1.17	– reactor and feeder fixed structure

- 1.18 – chain of the oscillating rotary system
- 1.19 – hydraulic motor of the oscillating rotary system
- 1.20 – micro switches
- 2 – coating in metals and special alloys
- 5 2.1 – body of the reactor
- 2.2 – flanges
- 2.3 – sealing ring of discharge cover (o-ring)
- 2.4 – sealing ring of bipartition (o-ring)
- 2.5 – vacuum sealing ring between shell and coating
- 10 2.6 – Ti ring for protection against Fe contamination in  
the Ti weld
- 3 – connections and valves of water, acidic solution, steam,  
vacuum, and pre-hydrolysate
- 3.1 – inlet for water and acidic solution
- 15 3.2 – inlet for steam
- 3.3 – outlet for steam
- 3.4 – vacuum
- 3.4.1 – vacuum in the reactor body
- 3.4.2 – vacuum in the conical sector
- 20 3.4.3 – vacuum in the reactor cover
- 3.4.4 – vacuum in the vacuum pump
- 3.5 – discharge of pre-hydrolysate

- 3.6 – valve for collection of pre-hydrolysate for analysis
- 3.7 – steam return valve in the perforated plate of the  
pre-hydrolysate discharge pipe
- 3.8 – steam return valve in the perforated tube of the steam outlet
- 5 4 – – entry support of the flexible rotation tubes
- 5 – – flexible rotation tubes
- 5.1 –water and acidic solution inlet
- 5.2 – steam inlet
- 5.3 – steam outlet
- 10 5.4 – vacuum
- 6 – – support for outlet of flexible tubes
- 7 – – intermediate piping
- 7.1 –water and acidic solution inlet
- 7.2 – steam inlet
- 15 7.3 – steam inlet
- 7.4 – vacuum
- 8 – flexible tilting tubes
- 8.1 – steam and acidic solution inlet
- 8.2 – steam inlet
- 20 8.3 – steam outlet
- 8.4 – vacuum
- 9 – piping and valves for water, acidic solution, steam and vacuum

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- 9.1 –water and acidic solution inlet
- 9.2 – steam inlet
- 9.3 – steam outlet
- 9.4 – vacuum
- 5 9.5 – valve piping assembly
- 10 – sensors
- 10.1 – in the body of the reactor
- 10.2 – in the conical sector
- 10.3 – in the reactor cover
- 10 10.4 – in the vacuum pump
- 11 – pressure gauge
- 12 – temperature gauge
- 13 – hydraulic systems
- 14 – feeder
- 15 14.1 – hydraulic motor
- 14.2 – propellor half-shaft
- 14.3 – feeder propellor
- 14.4 – cradle of the feeder
- 14.5 – conical feeder nozzle
- 20 14.6 – cap
- 15 – vacuum pump
- 16 – control panel (liquids, vapors, meters, electric systems, etc.)

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17 – leakage detector

18 – Cart – Capacity 30 t

**B – 2nd Structure (2nd cart – figures not included)**

19 – heat exchanger

5 20 – pressure pump (20.1) for water and acidic solution (20.2)

21 – water deionizer

22 – boiler

23 – support structure for items 19 to 22

**Processing of Pre-Hydrolysis of Biomass and Resulting Products**

10 The pre-hydrolysis may be carried out in any type of biomass, such as wood, and sugar-cane bagasse and straw, vegetable residues, barks, grass, organic part of garbage, etc. The pre-hydrolysis process follows these steps:

1- The biomass in minced form is discharged on the feeding platform, which may be constituted by a conveyer or inclined helical feeder, where it is washed in order to diminish  
15 the inorganic content (earth, ashes, etc.).

2- The feeding platform unloads the biomass into the helical feeder, which fills the reactor until the beginning of the compacting, reaching the density of 300 kg/m<sup>3</sup> (dry matter), which is three times the density of soft biomass (bagasse, straws, grass, vegetable residues, barks, organic part of garbage). The feeder remains coupled to the reactor during the filling  
20 operation, which lasts about 10 minutes. After the reactor has been filled, it is uncoupled from the feeder by a horizontal movement of the movable structure with respect to the fixed structure. After the uncoupling, the inlet nozzle is closed by a valve commanded by hydraulic cylinders.

3- After the reactor has been filled, the degasifying operation begins by passing  
25 steam, flooding the reactor with a acidic solution (on the order of 1.7% of the biomass), pre-heated up to 80° C in the heat exchanger and in the liquid/solid ratio - L/S = 2, heating and pressurizing up to 160° C, 0.62 MPa. This activity has a duration of 10 minutes, and the heat of the escape steam is recovered in the heat exchanger by the acidic solution of the next re-

action. In order to carry out this recovery of heat, the heat exchanger is usually sized with twice the volume of acidic solution required for each reaction.

4- After heating and pressurizing, the pre-hydrolysis is carried out for a period of 30 minutes simultaneously with the rotary oscillation of the reactor and purge of steam, in order to maintain the temperature close to  $160^{\circ}\text{C} \pm 10^{\circ}\text{C}$ , which is fundamental to obtain the characteristic of catalytic combustion of cellulignin, since the lower temperatures do not hydrolyze completely the memicellulose and amorphous cellulose, and higher temperatures cause the transformation of crystalline cellulose into amorphous cellulose, thus making it difficult to grind it into fine particles ( $f < 250\text{mm}$ ). It should be noticed the importance of the flexible connections to maintain the temperature during the whole period of hydrolysis and the oscillation of the reactor to renew the limit layer of the liquid saturated with sugar on the surface of the chops or particles of biomass, optimizing the hydrolysis period by about 20 - 30 minutes. The control of the pre-hydrolysis is made by accompanying the sugar content in the pre-hydrolysate by means of the refractometer or any other sugar-measuring apparatus up to the value of 9 Bricks. Longer periods of pre-hydrolysis result in a drop of the sugar content due to the decomposition of the xylose into furfural and furfurylic alcohol. The complete control of temperature, pressure, acid content, oscillation (homogenization) and purity of steam permits complete optimization of the pre-hydrolysis process.

5- After the pre-hydrolysis the operation of discharging the pre-hydrolysate (sugar solution) begins, which is directed to the stationary tank or tank-cart through the heat exchanger, thus recovering its energy in the pre-heating of the acidic solution and in the boiler water. The recovery of the heat of the pre-hydrolysate from the escape steam (heating and purge), and the use of low liquid/solid ratio ( $L/S=2$ ) allows one to reduce the consumption of energy of this invention to values lower than 6% of the energy contained in the original biomass. These values are significantly lower than in any other biomass processing, which in most cases are on the order of 30% ( $L/S=12$  ratio). The operation of discharge of the hydrolysate lasts about 10 minutes.

6- After the discharge of the pre-hydrolysate, the sugar-recovering washing is carried out in the proportion  $L/S = 1$ , aiming at a Brick  $\geq 5$ . This second fraction of the pre-hydrolysate may or may not be mixed in the first fraction (Brick  $\geq 9$ ). In general, the first fraction should be intended for the production of furfural (highest possible concentration of sugar), and the second fraction for the production of alcohol (for example, by fermentation with *engineered echerichia coli*). Note that the second fraction contains

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processes with a high consumption of water ( $L/S = 12$ ) one has never considered the use of deionized water and, consequently, the use of cellulignin as a fuel for gas turbines.

The biomass pre-hydrolysis process executed by the Failsafe-Type reactor generates two products (two commodities): cellulignin and pre-hydrolysate.

5

## CELLULIGNIN

As regards cellulignin, it should be noted that wood is composed of hemicellulose, cellulose and lignin disposed in microfibrillae. The objective of the pre-hydrolysis executed in the Failsafe-Type reactor is to digest the hemicellulose and amorphous cellulose, leaving the cellulose intact in its crystalline form and the lignin in the globulized form. All these features have been achieved and shown in the microphotograph of figure 3. This microphotograph shows the fractal of the fibers of crystalline cellulose with the globulized cellulignin, where the empty spaces were occupied by the hemicellulose and amorphous cellulose prior to the pre-hydrolysis.

This result has the following characteristics:

15

a) due to the complete control of the process parameters of the Failsafe-Type reactor, the characteristics are uniform throughout the mass of the reactor, enabling the production of "homogeneous commodities".

20

b) Due to the maintenance of the crystallinity, it is possible to grind the cellulignin into particles smaller than 250  $\mu$ m in hammer grinders, pin grinders and the like, with a consumption of energy of 12 kWh/t, which applied to Bond's formula:  $W=10 \log_{10} \frac{W_i}{P}$  whence  $W$  = work in kWh/t,  $W_i$  = rate of work of the material,  $P$  = mesh size through which 80% of the product (in microns) passes,  $F$  = mesh size through which 80% of the feed material passes (in microns) results in  $W_i = 15$ , which is the same order of most mineral materials (that is to say, crystallines). The cost of the grinding energy is lower than US\$ 1.00/t.

25

c) Due to the high porosity, the cellulignin undergoes a dry by natural gravity to content of 50% of moisture, dispensing with expensive screws presses for this processing step. The final drying is made in rotary dryers, achieving moisture lower than 12% with the same consumption of energy of the drying of cereals (750 MJ/t), illustrated by the examples below:

c.1) drying of cellulignin: consumption of 0.4 kg/h of GLP (42 MJ/kg of calorific power) during 10 hours to dry 224 kg of cellulignin -  $(0.4 \times 10 \times 42) / 0.224 = 750 \text{ MJ/t cellulignin}$ ;

c.2) drying of rice: consumption of 1/3 stere (cubic meter) of wood (396 kg/stere, 10.5 MJ/kg of calorific power) to dry 30 sacks of rice a day, 60 kg/sack) -  $(0.33 \times 396 \times 10.5) / 1.8 \cong 760 \text{ MJ/t rice}$ .

The cost of drying using noble fuels (wood - US \$10.00/stere - US\$1.80/t of cellulignin or GLP - US\$ 0.50/kg - US\$ 9.00/t of cellulignin) is always very expensive, and so one should use residual heat at 125°C of the boilers. As a result, the drying and grinding should always be made close to the thermoelectric station or boiler, using residual heat;

d) Due to the globulization of lignin, empty spaces are opened for attack of the cellulose by microorganisms of ruminant animals, and the cellulignin may be used as a volume component of animal forage with digestibility of 58% comparable to high quality volume components (wet maize silage - 61%, alfalfa silage - 56%, grass forage - 56%, oat straw - 44%, and much higher than the digestibility of natural grass (35%).

e) The greatest application of cellulignin is as fuel for boiler, gas turbine and generation of power by magnetohydrodynamics (MHD). Table 6 gives an example of application of cellulignin as fuel for boiler, as compared with fuel oil. The lower calorific power of cellulignin (20 MJ/kg), compared with that of the fuel oil (41 MJ/kg), is counterbalanced by its cost (US\$ 40.00/t), which is 1/3 lower than that of oil (US\$ 120.00/t). Although twice as much cellulignin is required, it is possible for one merely to replace the fuel oil in any type of boiler, since it is an oxygenated fuel (29% of O<sub>2</sub>) and requires insufflation of air with volumes close to that of the fuel oil. This means that any oil or gas boiler is capable of burning cellulignin, generating the same thermal power with adjusts on the order of 15% of the burners and air insufflators. The cellulignin produced with deionized water meets the requirements of clean fuel for burning in gas turbines with content of Na + K < 5 ppm. Although the clean cellulignin contains values < 15 ppm, these values are reduced by the cleaning cyclone. For particles smaller than 200 mm, the burning thereof is of the catalytic type, as shown in figure 4. This characteristic results from two factors, the first one being due to the large exposed surface (2 m<sup>2</sup>/g measured by BET - Brunaur, Emmett and Tellen or the number of iodine 100), compared to the surface of natural biomass (0.4 m<sup>2</sup>/g), and the second one being due to its grinding into fine particles ( $f < 250 \text{ mm}$ ), bringing about the entry of carburant oxygen and the exit of the monoxide in the pores of the cellulignin, without collision between the molecules, giving way to the catalytic combustion (size of cellulignin particle < average free way of the

carburant and gases from the combustion). All indicates that cellulignin is the only solid catalytic fuel that can be produced on a large scale, its period of combustion (< 20 milliseconds) being on the same order as that of natural gas. Gas turbines also require total particulate content < 200 ppm and particulates bigger than 5 mm < 8 ppm. These characteristics are achieved by means of three techniques: complete combustion due to the catalytic characteristic of cellulignin, cyclone installed between the external combustor and the gas turbine and magnetic separator after the grinding of the cellulignin to remove the magnetic contamination originated from the grinders. Without magnetic separators, one reaches values < 50 ppm of total particulates and using magnetic separation one reaches the requirement of 8 ppm < 5 mm. Due to the catalytic combustion, cellulignin is an excellent fuel for MHD, achieving high electric conductivity in the plasma of combustion at high temperature of 2727° C (3.000 K). Figure 5 shows the electric conductivity on the order of 70 S/m, compared with the values of 15 S/m for purified mineral coal, 12 S/m for oil derived from petroleum and 8 S/m for natural gas. It should be noted that wood has carbon content of 48% and hydrogen content of 6%, giving a ratio of C/H = 8. The pre-hydrolysis raises the carbon content in cellulignin to 66% and lowers the H content to 4.3%, doubling the ratio C/H = 15.

**Table 6 – Comparison of Oil and Cellulignin Burning in a Conventional Boiler**

Project Data			
Projected pressure		7.4 Mpa	
Maximum continuous steam flow – Gauge		67,000 kg/h	
Maximum steam pressure – Gauge		6.5 Mpa	
Steam temperature		485°C	
Feed water temperature		180°C	
Exhaust system		Balanced	
Fuel Data			
Composition (% by weight)	Oil (APF-AI)	Cellulignin	
		Normal <sup>(a)</sup>	Clean <sup>(b)</sup>
Carbon	87.04	66.20	66.30
Hydrogen	11.12	4.30	4.30
Sulphur	0.04	0.10	< 0.01
Nitrogen	0.30	--	--
Oxygen	1.50	29.30	29.40
Ashes	--	0.10	< 15 (Na+K) <sup>(c)</sup>
Higher calorific power	43.7	20.7	20.7
Lower calorific power	41.2	19.8	19.8
(a) Produced with non-deionized water; (b) Produced with deionized water; (c) Values in ppm.			

Cont. Table 6

Fuel Data		
Fuel	Oil	Cellulignin <sup>(d)</sup>
Maximum continuous evaporation rate (kg/h)	67,000	60,300
Steam pressure gauge (Mpa)	6.5	6.5
Steam temperature (°C)	485	485
Feed water temperature (°C)	180	180
Gas temperature at the pre-heater outlet (°C)	180	200
Room temperature of the air (°C)	25	25
Main fuel flow (kg/h)	4,687	8,770
Auxiliary fuel flow of (kg/h)	—	186 <sup>(e)</sup>
Air flow (kg/h)	73,800	84,710
Gas flow (kg/h)	84,040	100,000
Excess air in the combustion (%)	20	13/30 <sup>(f)</sup>
Efficiency (Base PCI) (%)	90.7	86.5
(d) Normal; (e) Natural gas or diesel oil; (f) 13% for cellulignin, 30% for the support		

Table 7 – main inorganic impurities of the eucalyptus and pre-hydrolysat

mg/g	Ca	K	Na	Mg	P	Al	Si	Mn	Fe	Zn	S
Eucalyptus	700	250	--	150	100	50	30	10	8	3	70
Clean cellulignin	1	15	--	80	2	40	100	2	8	--	80
Pre-hydrolysate	280	420	80	160	90	15	30	25	40	5	2,500

5 This result is highly significant, since figure 5 shows that the electric conductivity is very low for low values of C/H, and increases significantly up to C/H = 15, saturating from now onwards. During the combustion, the hydrogen forms the hydroxyl OH<sup>+</sup>, which has a shock section of 400 Å for the electron in the combustion plasma, decreasing its electric conductivity and failing to influence its value to content lower than 3% of H.

10 f) In addition to the applications as fuel and volume component for animal forage, cellulignin has various applications in the following areas: pyrolysis for the production of oils and activated coal, production of carbon black (incomplete combustion), production of methanol, cellulignin resins (agglomerates, MDF - Medium Density Fiber), substrate for semi-solid fermentation (fungi, bacteria and enzymes), etc.

## 15 PRE-HYDROLYSATE

The pre-hydrolysate is a solution of sugars containing xylose (80%), glucose, mannose, galactose, arabinose, acetyls, uranic acids, etc. In addition to the sugars, it con-

tains sulfuric acid added in the pre-hydrolysis process and inorganic impurities given in Table 7. The high control of process of the Failsafe-Type reactor allows one to carry out a virtually perfect pre-hydrolysis, permitting the digestion of all the products that are easily hydrolyzable, while preventing the decomposition of the sugars due to the low temperature of the process

5 (160° C). The content of soluble sugars (Bricks) is follow minute by minute, and the process is discontinued (beginning of the discharge, depressurization, cooling) as soon as the Bricks passes by a maximum. The low L/S ratio = 2 allows one to achieve sugars content on the order of 10 Bricks similar to other broths (cane, maize, etc.). The pre-hydrolysate in general has pH = 1. The recovery of sugars (type of washing with L/S = 1) generates a pre-

10 hydrolysate with Bricks on the order of 5 an pH = 1.5, which may be mixed with the former or not, for further processing.

The pre-hydrolysate has three main applications: production of furfural by the two-state technique (dehydration of pentoses), production of ethanol (*engineered echerichia coli* bacterium) and production of xylitol (catalytic hydrogenation of D. xylose).

15 It should be understood that the example of reactor described together with the values mentioned are only illustrative and does not limit the protection scope of the invention.

# Claims

1. An apparatus for pre-hydrolysis of biomass comprising:

- an external coating (1),

5      - an internal coating (2), the internal coating (2) covering the inside of the external coating (1);

- there being a space between the internal coating (2) and the external coating (1), said apparatus being characterized in that vacuum (3.4) is produced in the space between the internal coating (2) and the external coating (1).

10      2. An apparatus according to claim 1, characterized in that it includes an oscillation mechanism.

3. An apparatus according to claim 2, characterized in that the oscillation mechanism enables the apparatus to oscillate around its horizontally arranged axis.

4. An apparatus according to claim 3, characterized in that the oscillation mechanism permits oscillation in an alternate way at equal intervals.

15      5. An apparatus according to claim 1, characterized in that the vacuum produced is below 1mm of Hg.

6. An apparatus according to claim 1, characterized in that it is a reactor.

7. An apparatus according to any one of claims 1 - 6, characterized in that the external coating (1) and the internal coating (2) are made of corrosion resistant material.

20      8. An apparatus according to any one of claims 1, 6 or 7, characterized in that its external coating (1) and internal coating (2) are made of microbonded carbon steel and refractory material, respectively.

25      9. An apparatus according to any one of claims 1, 6, 7 or 8, characterized in that the external coating (1) and the internal coating (2) are mounted by simple juxtaposition, free from welding.

10. An apparatus according to any one of claims 1 - 9, characterized by comprising devices for detecting and monitoring the vacuum between the external coating (1) and the internal coating (2).

5 11. An apparatus according to claim 10, characterized in that the detection and monitoring devices detect vacuum microleakage, so as to enable one to detect microcracks in the internal coating (2).

12. An apparatus according to any one of claims 10 or 11, characterized in that the detection of microcracks is made in a continuous way.

10 13. An apparatus according to any one of claims 10 - 12, characterized in that helium gas is introduced into the reactor for detection of microcracks in the internal coating.

14. An apparatus according to any one of claims 7 - 10, characterized in that the microleakage detectors are coupled to the vacuum pump (15).

15. A biomass pre-hydrolysis process comprising the following steps:

- discharging of the biomass into the helical feeder;

15 - starting, in the biomass pre-hydrolysis device, the operation of pressurization, which comprises the following steps:

b.1) flooding the biomass pre-hydrolysis device with a pre-heated acidic solution;

b.2) heating; and b.3) pressurizing;

20 c) said process being characterized in that the pre-hydrolysis is carried out simultaneously with the rotary oscillation of the biomass pre-hydrolysis apparatus, purging of the steam and controlling of temperature, pressure, acid content, time of pre-hydrolysis, and liquid/solid ratio;

d) accompanying the sugar content up to a value close to 10 bricks by means of a sugar meter;

25 e) discharging the pre-hydrolysate in the tank through the heat exchanger;

f) sugar-recovery washing; and

g) discharging the cellulignin into mechanical washers or carts to be washed by percolation.

16. A process according to claim 15, characterized in that the filling of the biomass pre-hydrolysis device is carried out by compacting the biomass in the pre-hydrolysis device.

17. A process according to claims 15 or 16, characterized in that the purging of steam from the pre-hydrolysis device maintains the temperature around 150° C - 170° C.

18. A process according to any one of claims 15, 16, or 17, characterized in that the purging of steam from the pre-hydrolysis device maintains the temperature preferably around 106° C.

19. A process according to any one of claims 15 - 18, characterized in that the pre-hydrolysis is effected during about 30 minutes simultaneously with oscillation and purging of steam.

20. A process according to claim 15, characterized in that the feeding of biomass is carried out on the feeding platform, constituted by an inclined helical conveyor.

21. A process according to claim 15, characterized in that the filling of the biomass pre-hydrolysis device is carried out by the helical feeder as far as the start of compaction, so as to achieve a density around 300 kg/m<sup>3</sup>.

22. A process according to claim 15, characterized in that the flooding of the biomass pre-hydrolysis device is made with an acidic solution corresponding to 1.7% of the biomass, is pre-heated up to approximately 80° C in the heat exchanger and in the liquid/solid ratio = 2 with heating between 150° C and 170°C, preferably 160°C and pressurization of about 0.62 MPa.

23. A process according to claim 15, characterized in that the heat of the escape steam in the degasing is recovered in the heat exchanger by the acidic solution of the following reaction.

24. A process according to claim 15, characterized by the use of filtered water in the process for producing normal cellulignin and deionized water in the process for producing clean cellulignin.



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25. A process according to claim 15, characterized in that the washing waters meet the specifications of fresh waters and may be discarded in any water stream.

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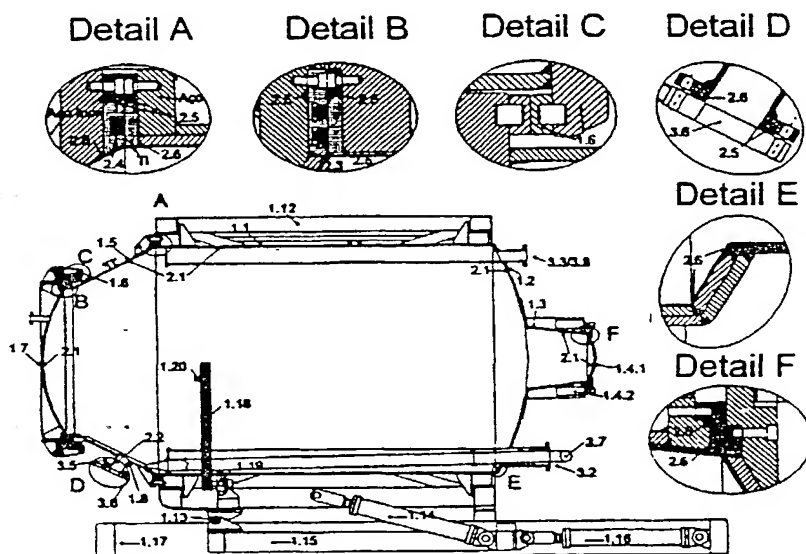
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[Continued on next page]

(54) Title: AN APPARATUS AND PROCESS FOR PRE-HYDROLYSIS OF BIOMASS



(57) Abstract: This invention refers to an apparatus for the processing of pre-hydrolysis of biomass, particularly a reactor of the failsafe type, either mobile or not, which may be manufactured of microbonded carbon steel and coated with special materials (refractory metals, superalloys, stainless materials, plastics, etc.). The insertion of vacuum between the shell of the reactor and its coating prevents its implosion and permits the detection of leakage with helium gas. The resistance to corrosion of the refractory metals enables carrying out of pre-hydrolysis and mineral digestion. In the process of this invention, biomass is compacted at 300 kg/m<sup>3</sup> by a helical feeder, degased, flooded, heated, stirred, pre-hydrolyzed, the sugar being recovered at a first washing within the reactor with values higher than 90 %.

The low liquid/solid ratio = 2 enables one to achieve sugar content of 10 bricks in the pre-hydrolysate and a consumption of 6 % of the energy contained in the processed biomass. The pre-hydrolysate is constituted by solutions of xylose and others and is intended for the production of furfural, alcohol and xylitol. The control of the process enables one to produce cellulignin with a high specific surface, 2 m<sup>2</sup>/g (measured by BET), compared with the value of 0.4 m<sup>2</sup>/g of non-hydrolyzed biomass, maintain crystallinity of the cellulose fibers, aiming at grinding it into fine particles ( $f < 250$   $\mu$ m), globulizing the lignin, exposing the cellulose to attacks by microorganisms from cud of ruminants, fungi, bacteria or enzymes in microbiological or enzymatic fermentation. The catalytic combustion due to the large specific surface results in a new fuel for boilers, combustors in general and MHD when produced with filtered water, and for gas turbines when produced with deionized water.

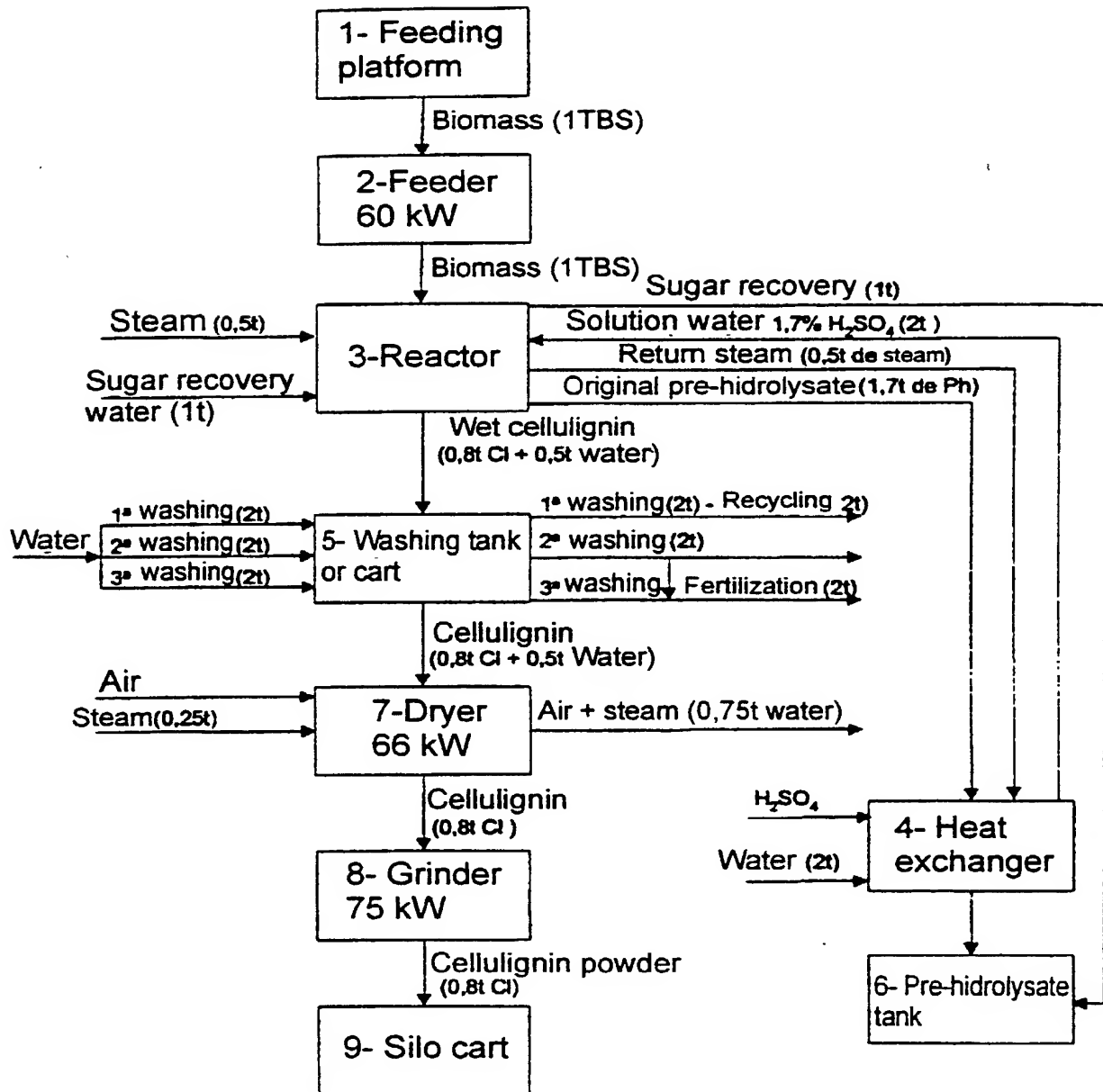
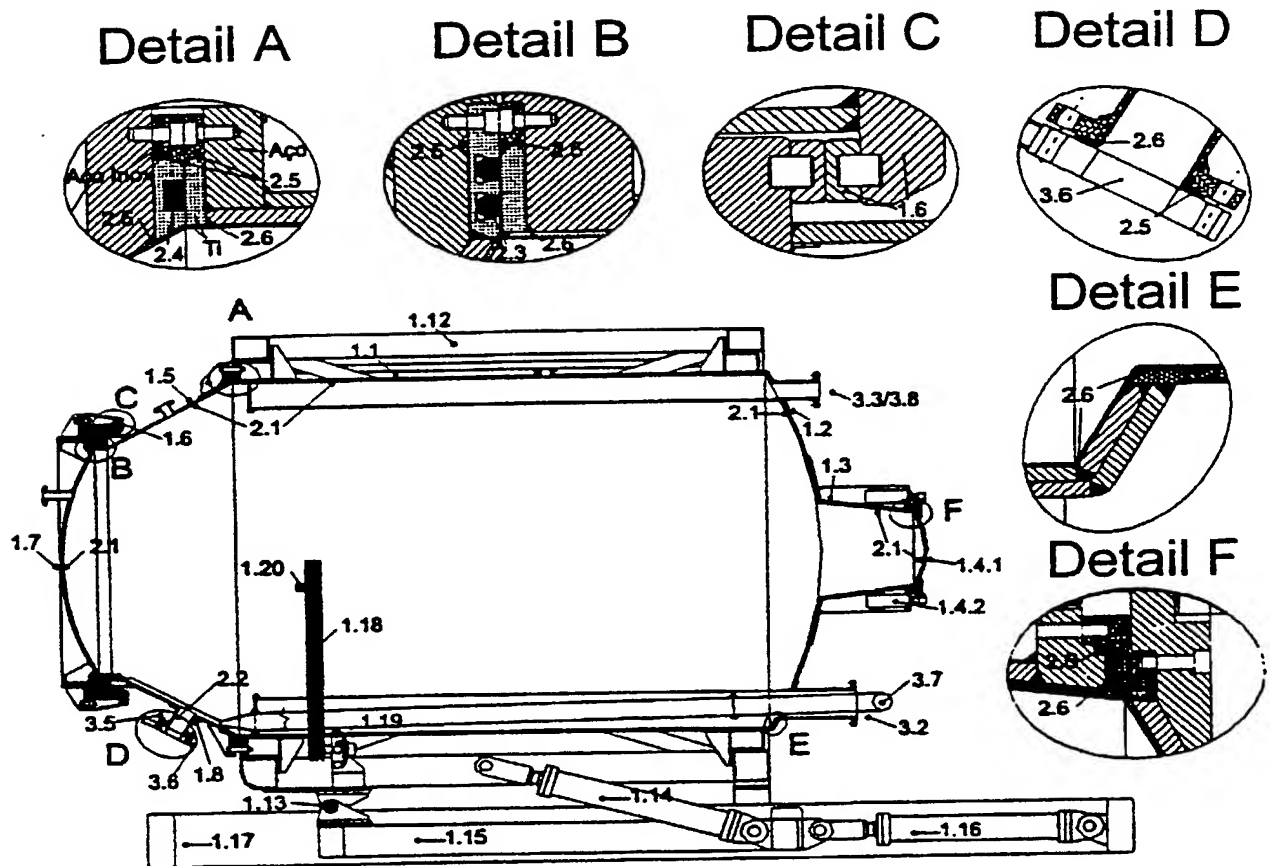


FIG. 1



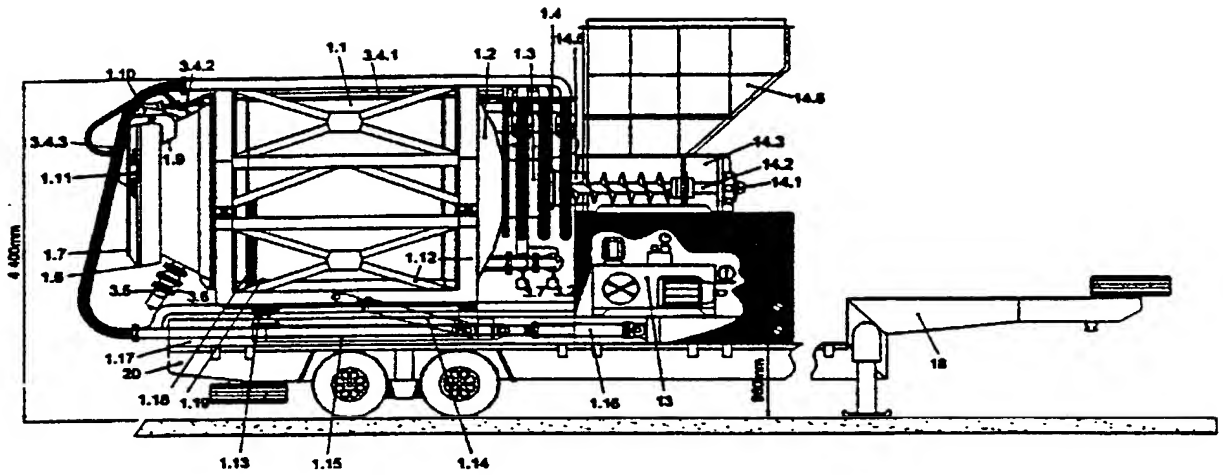


FIG. 2b

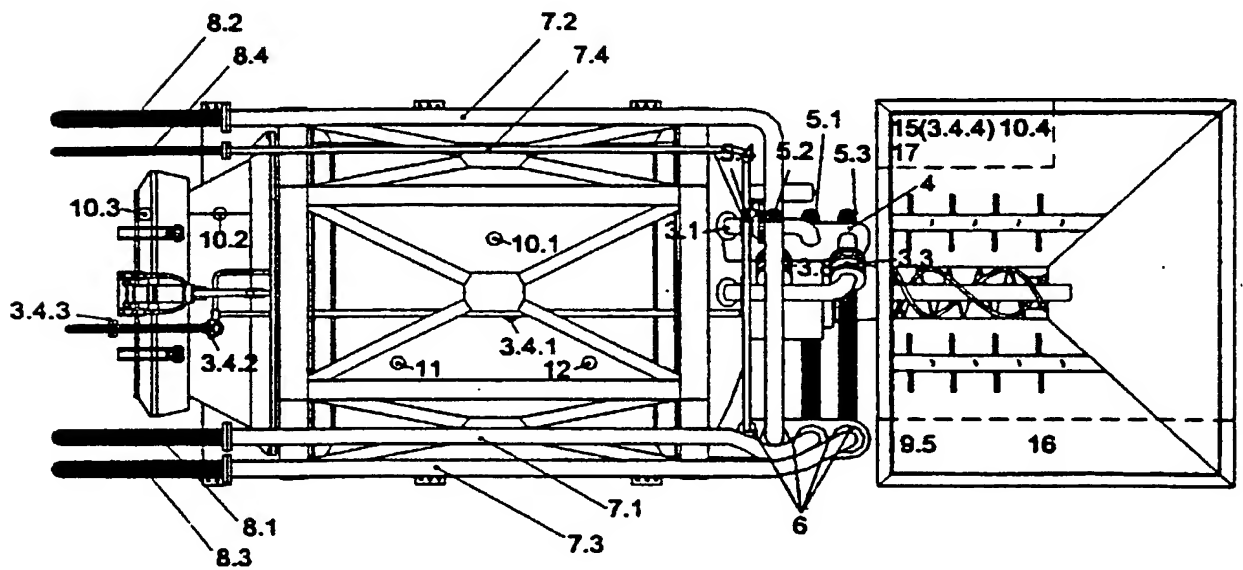


FIG. 2c

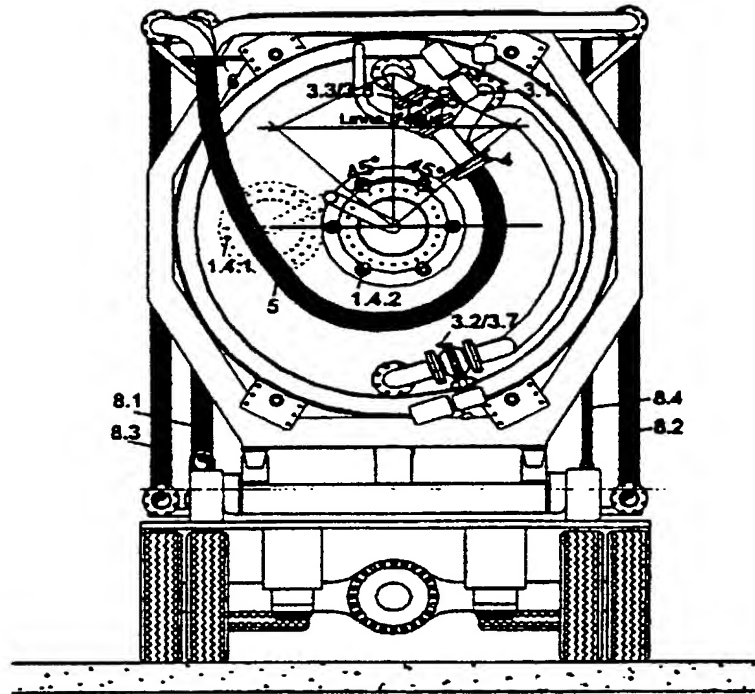


FIG. 2d

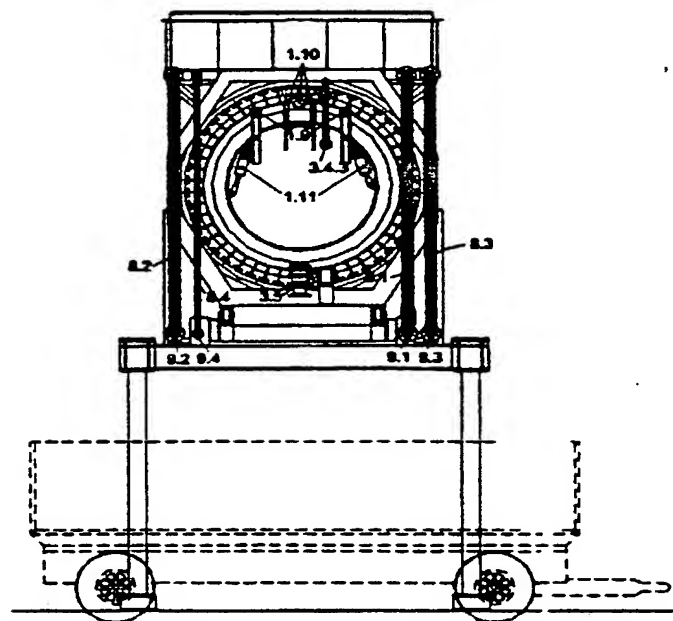
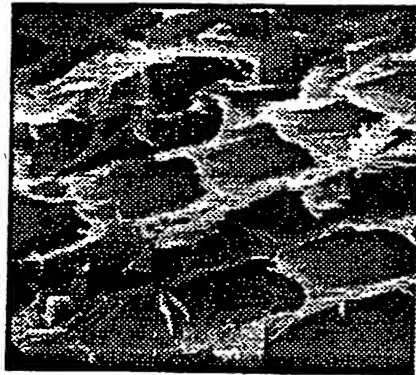


FIG. 2e



1800 X, 1 mm = 370 nm



5000 X, 1 mm = 133 nm

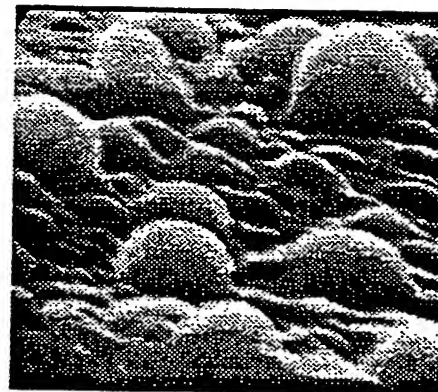
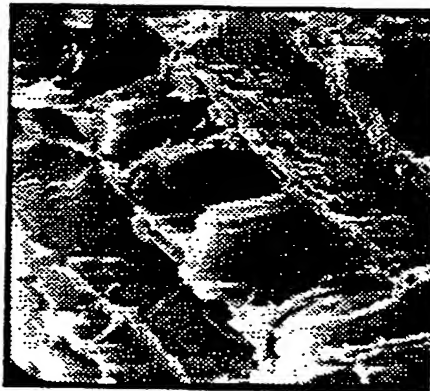


FIG. 3





## Declaration and Power of Attorney United States Patent Application

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**"An apparatus and process for pre-hydrolysis of biomass"**

the specification of which

(check one) ☐ is attached hereto.

☒ was filed on December 19, 2000 as U.S. Application Serial No. \_\_\_\_\_ and (if applicable) was amended on \_\_\_\_\_

☒ was filed as PCT International Application No. PCT/BR00/00065 on June 23, 2000 and (if applicable) was amended under PCT Article 19 on \_\_\_\_\_

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign and PCT application(s) for patent or inventor's certificate listed in this Declaration and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Foreign/PCT Application No.	Country	Filing Date	Priority Claimed? (yes/no)
PT 9902607-4	BR	23 June 1999	yes
PCT/BR00/00065	PCT	23 June 2000	yes

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) and PCT International Application(s) listed in this Declaration and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT International filing date of this application:

U.S. Application No.	Filing Date	Status (patented/pending/abandoned?)

I hereby appoint the following attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Joseph A. DeGrandi (17446), Robert G. Wellacher (20531), Richard G. Young (20628), Michael A. Mikuch (32263), Bernard A. Meany (22081), Helen M. McCarthy (32513), Dennis C. Rodgers (32936), William F. Rauchholz (34701), C. Byron Stover (34737), Thomas L. Evans (35805), Maurice U. Cahn (30454), Robert Jones Warrall (37569), and William J. Rudren (31712).

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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